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Corrosion inhibition by caffeine – Mn^{2+} system

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The inhibition efficiency of caffeine in controlling corrosion of carbon steel immersed in 60 ppm of Cl^- ion environment has been evaluated, in the absence and presence of Mn^{2+} ions, by weight loss method. Influence of sodium dodecyl sulphate, pH and immersion period on the inhibition efficiency of the caffeine-Mn^{2+} ion system has also been investigated. The protective film formed on the metal surface has been analysed by FTIR spectra. The protective film consists of Fe^{2+} - caffeine complex and $Mn(OH)_2$.

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Environment friendly inhibitors have attracted the attention of researchers. Non-toxic natural products have been widely used as corrosion inhibitors. Natural products such as tannins[1-3] have been used as inhibitors. Extracts of plants such as *Cerum petroselinum, Lupine*, *Doum* and *Orange* shells have been used as corrosion and scale inhibitors[4]. *Pomegranate*[5], *Swertia aungustifolia*[6] and *Azadiracta indica*[7] have shown good inhibition activity. The scale inhibition efficiencies of the aqueous extracts of plant materials, namely, *Cordia latifolia*, *Eucalyptus* and *Jasminum auriculatum* have been evaluated[8]. The present work (i) evaluates the inhibition efficiency of caffeine, a natural product in controlling corrosion of carbon steel, immersed in aqueous solution containing 60 ppm of Cl^- ion, in the absence and presence of Mn^{2+} ion, (ii) examines the influence of sodium dodecyl sulphate, pH and immersion period on the inhibition efficiency of the caffeine – Mn^{2+} ion system, (iii) analyses the protective film by fourier transform infra red spectra and (iv) proposes a suitable mechanism of corrosion inhibition.

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Experimental Procedure

Preparation of specimens

Mild steel specimens [iron containing S 0.026, P 0.06, Mn 0.4 and C 0.1%] of dimensions 1.0 × 4.0 × 0.2 cm were polished to a mirror finish, degreased with trichloroethylene and then used for the weight-loss method and surface examination studies.

Weight – loss method

Specimens, in triplicate, were immersed in 100 mL of the solutions containing 60 ppm of Cl^- (as NaCl) and various concentrations of the inhibitor in the absence and presence of Mn^{2+} (as manganese sulphate), for three days. The weight of the specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion inhibition efficiency (IE) was then calculated using the equation,

$$IE = 100\,[1 - W_2 / W_1]\ \%$$

where W_1 = corrosion rate in the absence of inhibitor

W_2 = corrosion rate in the presence of inhibitor

Surface examination study

The specimens were immersed in various test solutions for a period of three days. After three days,

the specimens were taken out and dried. Nature of the film formed on the surface of the metal specimens was analysed by FTIR spectroscopy.

FTIR spectra

The film formed on the metal surface was carefully removed, mixed thoroughly with KBr and made into pellets. These spectra (KBr) were recorded in Perkin Elmer – 1600 spectrophotometer.

Results and Discussion

Weight-loss method

The inhibition efficiency (IE) of caffeine, in controlling corrosion of carbon steel immersed in an aqueous environment containing 60 ppm of Cl^- ions, in the absence and presence of Mn^{2+} ions was evaluated by weight loss method.

Corrosion inhibition by caffeine

The corrosion rates of carbon steel when it is immersed in chloride environment in the presence of various concentrations of caffeine, for a period of 3 days, are given in Table 1. It is observed, that, as the concentration of caffeine increases the inhibition efficiency gradually increases and then decreases. A maximum of 38 percent IE is noted when the concentration of caffeine is 100 ppm.

Corrosion inhibition by Mn^{2+} ions

It is observed from Table 2, that, 25 ppm of Mn^{2+} ($MnSO_4.H_2O$) ions have 36% IE. As the concentration of Mn^{2+} ions increases, the IE slowly decreases.

Table 1 — Corrosion rates (CR) of carbon steel immersed in chloride ion environment for 3 days and the inhibition efficiency of caffeine

Inhibitor system : caffeine

Cl^- = 60 ppm

Sl No.	Caffeine (ppm)	CR (mdd)	IE (%)
1	—	20.22	—
2	25	16.90	16
3	50	16.10	20
4	75	14.00	31
5	100	12.50	38
6	125	14.00	30
7	150	14.60	28

Inhibition efficiency of the caffeine – Mn^{2+} ion systems

The inhibition efficiency of the caffeine – Mn^{2+} ion systems are given in Table 3. When 25 and 50 ppm of Mn^{2+} ions are added to various concentrations of caffeine, the inhibition efficiency gradually increases and then decreases. It is generally observed, that, when the concentration of Mn^{2+} ion is low, the caffeine-Mn^{2+} ion system shows a better IE. For example, 75 ppm of caffeine shows 36% IE in the presence of 50 ppm of Mn^{2+}, while it is 44% in the presence of 25 ppm of Mn^{2+}.

Table 2 — Corrosion rates of carbon steel immersed in chloride ion environment for 3 days and the inhibition efficiency of Mn^{2+} ion

Inhibitor system: Mn^{2+} ion

Cl^- = 60 ppm

Sl. No.	Mn^{2+} (ppm)	CR (mdd)	IE (%)
1	—	20.22	—
2	25	12.90	36
3	50	13.40	34
4	75	13.70	32
5	100	13.40	34
6	125	14.90	26
7	150	15.20	24

Table 3 — Inhibition efficiencies of the caffeine – Mn^{2+} ion systems, when carbon steel is immersed in 60 ppm of Cl^- ion environment for 3 days

Caffeine (ppm)	Inhibition efficiency (%) Mn^{2+} (ppm)		
	0	25	50
0	—	36	34
25	16	32	28
50	20	36	36
75	31	44	36
100	28	42	32
125	30	39	29
150	38	36	29

Inhibition efficiency of sodium dodecyl sulphate (SDS)

The inhibition efficiency of SDS, an anionic surfactant, is given in Table 4. It is observed that as the concentration of SDS increases, the IE also increases. At 100 ppm of SDS, maximum IE is observed and then it decreases. Up to 100 ppm of SDS, it exists as monomer. Adsorption of SDS on the carbon steel surface takes place through the oxygen atom of the sulphate group[9]. Above this concentration, several monomers of SDS assemble to form micelles and hence, the amount of SDS on the metal surface decreases. This leads to a decrease in the IE.

Influence of SDS on the inhibition efficiency

The formulation consisting of 75 ppm of caffeine and 25 ppm of Mn^{2+} has 44% IE. The influence of SDS, on the IE of this system is given in Table 5. It is observed that as the concentration of SDS increases, the IE first decreases and then gradually increases.

Table 4 — Inhibition efficiency of SDS

Cl^- = 60 ppm

Sl No.	SDS (ppm)	IE (%)
1	25	9
2	50	15
3	75	22
4	100	24
5	125	16
6	150	16

Table 5 — Influence of SDS on the inhibition efficiency of the caffeine – Mn^{2+} system

Cl^- 60 ppm; Caffeine, 75 ppm; and Mn^{2+}, 25 ppm

Sl No.	SDS (ppm)	IE (%)
1	0	44
2	25	38
3	50	41
4	75	42
5	100	48
6	125	48
7	150	55

Influence of immersion period on the inhibition efficiency

The influence of immersion period on caffeine — Mn^{2+} system is given in Table 6. It is observed that as the immersion period increases, the IE of the system decreases. This is because the protective film formed on the metal surface is continuously attacked by the Cl^- ions present in the environment.

Influence of pH on the inhibition efficiency

The influence of pH (addition of dilute H_2SO_4 or dilute NaOH solution) on the inhibition efficiency of the caffeine (75 ppm) – Mn^{2+} (25 ppm) ion system is given in Table 7. As the pH increases, the IE increases first and then decreases. A maximum of 44% IE is observed at pH 7. In the acidic medium and also in the basic medium, the protective film is destroyed. Moreover, in the basic medium, Mn^{2+} is precipitated as $Mn(OH)_2$. Hence Mn^{2+} ions are not able to reach the surface of the metal.

Analysis of FTIR spectra

The FTIR spectra are shown in Fig. 1. The FTIR spectrum of pure caffeine is shown in Fig.1a. The C=O stretching frequency appears at 1658 cm^{-1}. The bands due to aromatic C-H stretch appear at 3111.4 and 2953.88 cm^{-1}. The band at 1484.5 cm^{-1} is due to C=N ring stretching. The CH_3 group absorptions[10] $\delta_s CH_3$ in CH_3 – N appear at 1403 and 1429.8 cm^{-1}.

The FTIR spectrum of the film formed on the surface of metal after immersion in the solution consisting of 60 ppm of Cl^- and 75 ppm of caffeine is shown in Fig. 1b. The C=O stretching frequency has decreased from 1658 cm^{-1} to 1632 cm^{-1}. This is due to the shift of the electron cloud of C=O bond towards Fe^{2+} ion formed on the metal surface. This results in the formation of caffeine – Fe^{2+} complex on the metal surface. The C=N ring stretching has decreased from

Table 6 — Inhibition efficiency of the caffeine (75 ppm) — Mn^{2+} (25 ppm) system as a function of immersion period

Immersion period (DAP)	1	3	5	7
IE (%)	48	44	7	0

Table 7 — Influence of pH on the inhibition efficiency of the caffeine (75 ppm) – Mn^{2+} (25 ppm) system

pH	3	5	7	9	11
IE (%)	-8	9	44	6	11

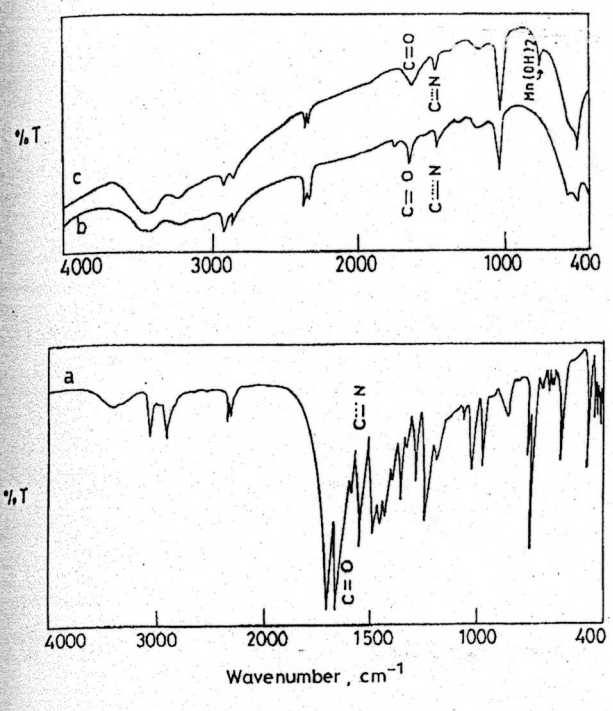

Fig 1 — FTIR spectra of pure caffeine and that of film formed on carbon steel after immersion in various test solution; (a) pure caffeine; (b) Cl^- 60 ppm + caffeine 75 ppm; (c) Cl^- 60 ppm + caffeine 75 ppm + Mn^{2+} ion 25 ppm

1484.5 cm^{-1} to 1454 cm^{-1}. This suggests that the electron cloud of C=N bond coordinates with Fe^{2+} ion formed on the metal surface. Thus, FTIR spectral study leads to the conclusion that in the presence of Cl^- and caffeine, the anodic reaction of metallic dissolution

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

is controlled by the formation of caffeine – Fe^{2+} complex on the anodic sites of the metal surface. Caffeine is coordinated to Fe^{2+} through the oxygen atom of the C=O group and the ring nitrogen.

The FTIR spectrum of the film formed on the surface of carbon steel after immersion in the solution containing 60 ppm of Cl^-, 75 ppm of caffeine and 25 ppm of Mn^{2+} ion is shown in Fig. 1c. The C=O stretching frequency has decreased from 1658 cm^{-1} to 1625 cm^{-1}. This is due to the shift of the electron cloud of C=O bond towards Fe^{2+} ion formed on the metal surface. The C=N stretching frequency has decreased from 1484.5 cm^{-1} to 1461 cm^{-1}. This is due to the shift of the electron cloud of the C=N bond towards Fe^{2+} ion formed on the metal surface. These results suggest the formation of caffeine-Fe^{2+} complex on the anodic sites of the metal surface. Caffeine is coordinated to Fe^{2+} ion through O atom and N atom. The band at 756 cm^{-1} is due to $Mn(OH)_2$ formed on the cathodic sites of the metal surface. Thus, the cathodic reaction of generation of OH^-.

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

is controlled by the formation of $Mn(OH)_2$ on the cathodic sites.

$$Mn^{2+} + 2\,OH^- \longrightarrow Mn(OH)_2 \downarrow$$

Mechanism of corrosion inhibition

The weight loss study reveals that the system consisting of 75 ppm of caffeine and 25 ppm of Mn^{2+} shows 38 percent inhibition efficiency. FTIR spectrum reveals that the protective film consists of caffeine – Fe^{2+} complex and $Mn(OH)_2$. In order to explain these observations, the following mechanism of corrosion inhibition is proposed:

- When the environment consisting of 60 ppm of Cl^-, 75 ppm of caffeine and 25 ppm of Mn^{2+} ion is prepared, there is the formation of caffeine – Mn^{2+} complex.
- When carbon steel is introduced in this solution, there is diffusion of manganese-caffeine complex towards the metal surface.
- On the metal surface, manganese complex is converted into iron complex on the anodic sites.

  $$Mn^{2+}\text{-caffeine} + Fe^{2+} \longrightarrow Fe^{2+}\text{-caffeine} + Mn^{2+}$$

- The released Mn^{2+} ion combines with OH^- to form $Mn(OH)_2$ on the cathodic site.

  $$Mn^{2+} + 2\,OH^- \longrightarrow Mn(OH)_2$$

- Thus, the protective film consists of Fe^{2+} - caffeine complex and $Mn(OH)_2$.

Conclusions

The corrosion rates of carbon steel immersed in Cl^- ion environment in the absence and presence of caffeine and Mn^{2+} have been evaluated. The present study leads to the following conclusions:

- 25 ppm of Mn^{2+} ion has 36% inhibition efficiency (IE). As the concentration of Mn^{2+} ion increases, IE decreases.
- Caffeine has some IE in controlling corrosion of carbon steel. As the concentration of caffeine increases, the IE first increases and then decreases.

- The study of the IE of the caffeine–Mn^{2+} system reveals, that, caffeine shows better IE in the presence of 25 ppm of Mn^{2+} ions than in the presence of 50 ppm of Mn^{2+} ions.
- In general, as the concentration of Mn^{2+} ions is increased, the IE of caffeine system gradually increases and then decreases.
- When various concentrations of sodium dodecyl sulphate are added to the caffeine–Mn^{2+} system, the IE first decreases and then gradually increases.
- As the period of immersion increases, the IE of the caffeine–Mn^{2+} ion system decreases.
- As the value of pH increases, the IE of the caffeine–Mn^{2+} ion system increases; maximum IE is attained at pH 7. Further increase in pH value lowers the IE.

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